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Magnetic Relaxation in Fe_3O_4 and Ferrites

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Magnetic permeability and loss tangent (tan δ) of Fe_3O_4 and some ferrites were measured in the frequency range of 100 kHz to 1 MHz and the temperature range of 4.2 to 300 K with a transformer bridge by using the three terminal method. While γ-Fe_2O_3 which has no Fe^{2+} ion showed no peak in tan δ-T curve, Fe_3O_4 showed a peak in tan δ near 40 K. MnZn ferrite with Fe^{2+} ions showed two peaks in tan δ near 30 and 150 K. The peak near 30 K was considered to be caused by the hopping of electron between Fe^{2+} and Fe^{3+} ions and the peak near 150 K by the electronic process of Mn ions.

INTRODUCTION

The Richter type magnetic relaxation[1] has been known in iron metal containing impurity carbon atoms. Interstitial carbon atoms change their positions with the magnetic field direction. The magnetic relaxations in MnZn ferrites observed at about 160 K have been explained by this type of magnetic relaxation process,[2,3] in which electrons transfer between Fe^{2+} and Fe^{3+} ions on the octahedral sites in the spinel structure. The change of the magnetic order with the magnetic field direction is achieved by the transfer of electron between these two ions. $Co_x Fe_{3-x}O_4$ cooled in the magnetic field has superior properties as a permanent magnet.[4] Directional order arrangement of Co ions causes this effect. This magnetic annealing effect and the magnetic relaxation mentioned above are originated in the same mechanism. In ferromagnetic resonance (FMR) the line width varies with temperature. The ferrites with ferrous ions show a maximum in the linewidth (ΔH) at 110 K[5]. In the single crystal of NiZn ferrite ΔH is the largest for [111] direction and decreases in order of [110] and [100]. This relaxation of FMR was explained by the transfer of electron between Fe^{2+} and Fe^{3+} on the octahedral sites. In $Mn_xFe_yO_4$, however, maxima of linewidth in FMR have been reported at 20 and 263 K[6]. The low temperature maximum was described by the slow relaxing ion mechanism of Mn^{3+}.

The previous paper[7] reported the dielectric relaxation of ferrites at low temperatures (about 30 K) arising from the transfer of electron between Fe^{2+} and Fe^{3+} ions on the octahedral sites in the spinel structure. In this paper we report the magnetic relaxation of these ferrites in the temperature range from 4.2 to 300 K measured with a transformer bridge by using the three terminal method. The magnetic relaxations corresponding to the dielectric relaxations were observed at the same temperature region. In MnZn ferrites

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another peak occurred at 160 K. The origin of these relaxations is discussed in terms of the dynamical process of electron.

EXPERIMENTALS

1. Sample Preparation

The precipitate Fe_3O_4 was formed by the oxidation of aqueous suspension of colloidal $Fe(OH)_2$ which was prepared by adding sodium hydroxide to ferrous sulphate solution.[8] The precipitates $Mn_xZn_yFe_{3-x-y}O_4$ were prepared by the same method. The sample of γ-Fe_2O_3 was obtained by oxidation of Fe_3O_4 powder in air at 300°C. These powder samples were confirmed to be of single phase by X-ray diffraction method. The powder samples were moulded with the binder of Araldite resin into a form of toroidal core and cured at 100°C. These pressed samples were measured for Fe_3O_4 and γ-Fe_2O_3. Sintered samples were prepared for $Mn_{0.47}$ $Zn_{0.48}$ $Fe_{2.05}$ O_4 and $Mn_{0.63}$ $Zn_{0.31}$ $Fe_{2.06}$ O_4 by calcination at high temperatures. The samples prepared by pressing with the Araldite binder had a size of 32 mm O. D. and 19 mm I. D. The size of a sintered ferrite sample was 25 mm O.D., 15 mm I.D., and 6 mm thick. The sintered MnZn ferrites of the above mentioned composition possesses exceedingly high permeabilities.

2. Measurements

Magnetic permeability and loss tangent are usually measured by the Maxwell bridge. In this bridge it is difficult to measure the inductance of a sample with a good accuracy in a cryostat far away from the bridge since errors due to stray capacity are unavoidable without using the Wagner arm. In this work complex inductance L^* was measured with an Ando Electric Co. TR-1B transformer bridge for measurements of capacitance and conductance. Some modifications were made for inductance measurement as shown in Fig. 1. Admit-

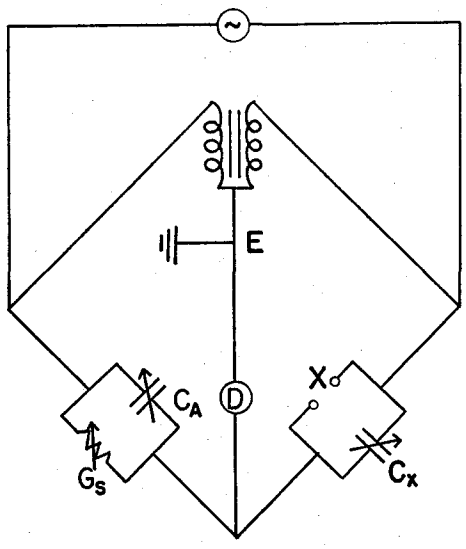


Fig. 1. A modified transformer bridge for inductance measurement. X, unknown terminal; C_X, 1pF-0.1 μF air capacitor; G_s, 3×10^{-5}–$10^4\mu\mho$ decade conductor; C_A, 1pF–0.1 μF air capacitor.

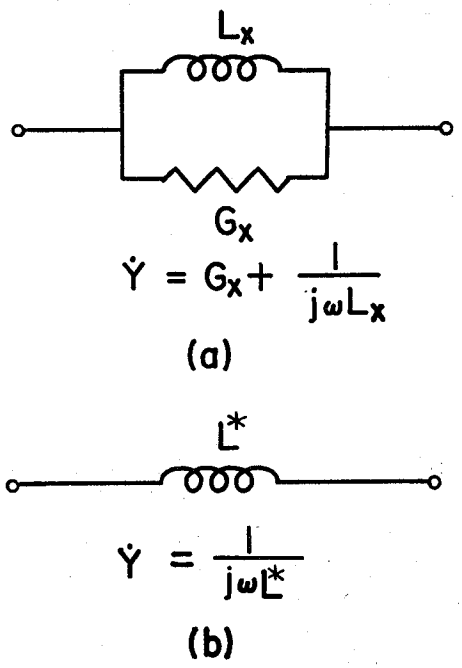


Fig. 2. Equivalent admittance of sample.
(a) L_X and G_X are the equivalent inductance and conductance in parallel of a sample coil, respectively.
(b) L^* is the complex inductance of a sample coil.

tance of sample (Fig. 2(a)) can be measured by the transformer bridge. At the balance of the bridge

$$G_X+\frac{1}{j\omega L_X}+j\omega C_X=G_S \tag{1}$$

The two conditions of balance are

$$G_X=G_S \tag{2}$$

$$L_X=\frac{1}{C_X\omega^2} \tag{3}$$

When the sample has the magnetic loss, the admittance of sample coil is given by $\frac{1}{j\omega L^*}$ (Fig. 2(b)).
Therefore,

$$\frac{1}{j\omega L^*}=G_X+\frac{1}{j\omega L_X} \tag{4}$$

The real and imaginary part, L' and L'', of the complex inductance L^* $(=L'-jL'')$ are

$$L'=\frac{L_X}{1+(G_X\omega L_X)^2} \tag{5}$$

$$L''=\frac{G_X\omega L_X^2}{1+(G_X\omega L_X)^2} \tag{6}$$

The magnetic loss tangent is written as

$$\tan\delta=\frac{L''}{L'}=\omega G_X L_X \tag{7}$$

The complex permeability $\mu^*=\mu'-j\mu''$ is given by the ratio of the complex inductance L^* to the inductance L_0 of the empty coil.

$$\mu'=\frac{L'}{L_0}=\frac{L_X}{L_0[1+(\tan\delta)^2]} \tag{8}$$

$$\mu''=\frac{L''}{L_0}=\frac{L_X\tan\delta}{L_0[1+(\tan\delta)^2]} \tag{9}$$

$$L_0=\frac{4n^2A}{D}\times 10^9 \tag{10}$$

where L_0 is H units, A and D are the cross section area in cm^2 and the mean diameter of the coil in cm and n means the number of turns of the sample coil. Errors due to stray capacity can be eliminated by the transformer arm and the measurement can be done independent of the length of cables from samples to the apparatus of measurement. Hence the sample placed in a cryostat far from the apparatus (about 1.5 m) could be measured precisely. Since the observed capacitance C_X for a value of L_X changes with a square of frequency (in Eq. (3)), the inductance L_X is observed in the limited frequency range. In this work inductance L_X was measured at frequencies of 100, 200, 500 kHz, and 1 MHz over the temperature range from 4.2 to 300 K.

RESULTS AND DISCUSSION

Figure 3 shows the temperature dependence of μ' and $\tan\delta$ of Fe_3O_4. A loss maximum is seen at about 40 K. The higher the frequency, the loss maximum appears at the higher

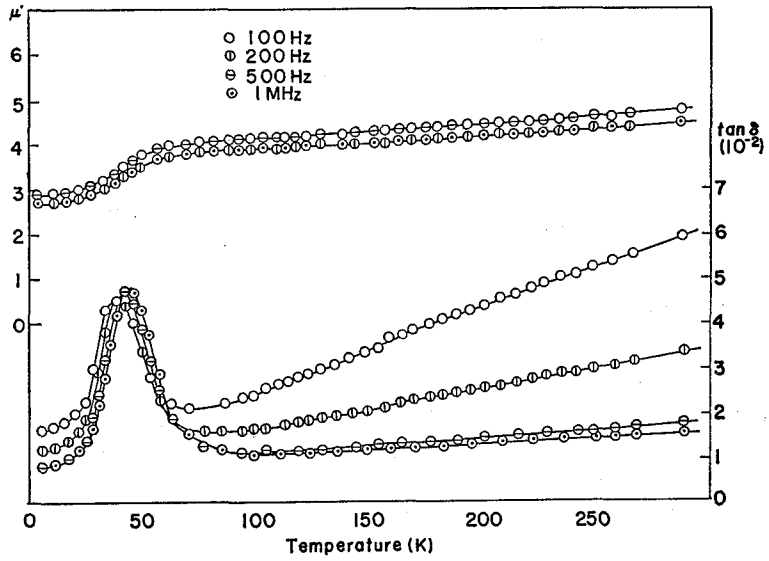


Fig. 3. Temperature dependence of permeability and loss tangent of Fe_3O_4.

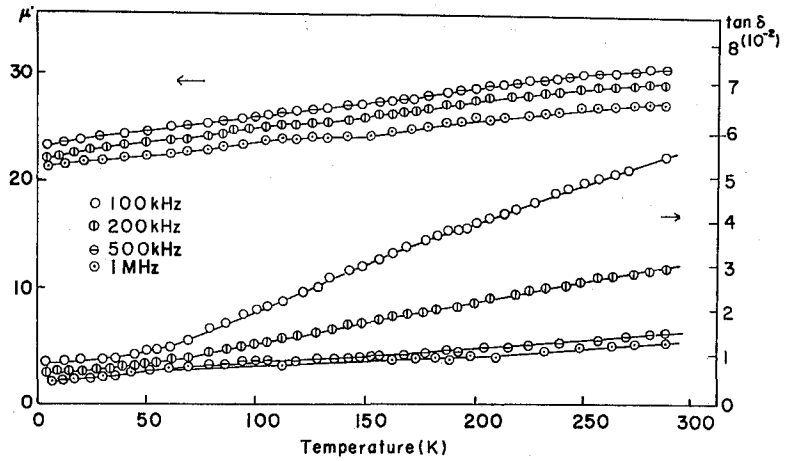


Fig. 4. Temperature dependence of permeability and loss tangent of γ-Fe_2O_3.

temperature. Temperature dependence of permeability and tan δ of γ-Fe_2O_3 are shown in Fig. 4. The value of tan δ changes slightly in all the temperature range of 4.2 to 300 K. This sample possesses small tan δ and permeability and has no magnetic relaxation as observed at about 40 K with Fe_3O_4. From this result it is supposed that the relaxation observed in Fe_3O_4 near 40 K is due to ferrous ions. MnZn ferrites have the exceedingly high permeability (Figs. 5 and 6). In Figs. 5 and 6 two magnetic relaxations are seen at 30 and 163 K. The relaxation near 30 K is considered to correspond to the one observed in Fe_3O_4. The relaxation at 163 K is seen only in the ferrites containing Mn ions and is considered to be due to Mn ions. H. P. J. Wijn *et al.*[2] have reported that the magnetic relaxation of $Mn_{0.66}Zn_{0.28}Fe_{2.06}O_4$ and $Ni_{0.49}Zn_{0.49}Fe_{2.02}O_4$ *etc.* observed at about 150 K are due to the electron hopping between Fe^{2+} and Fe^{3+} ions since the activation

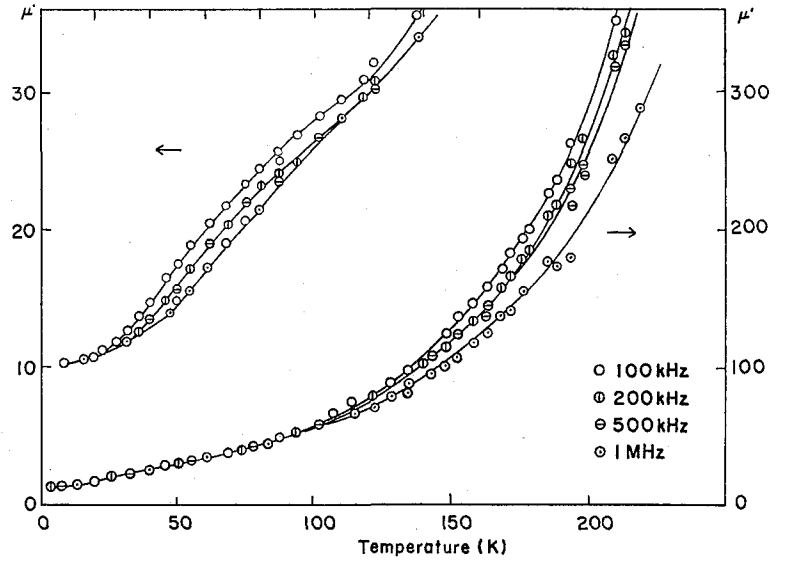
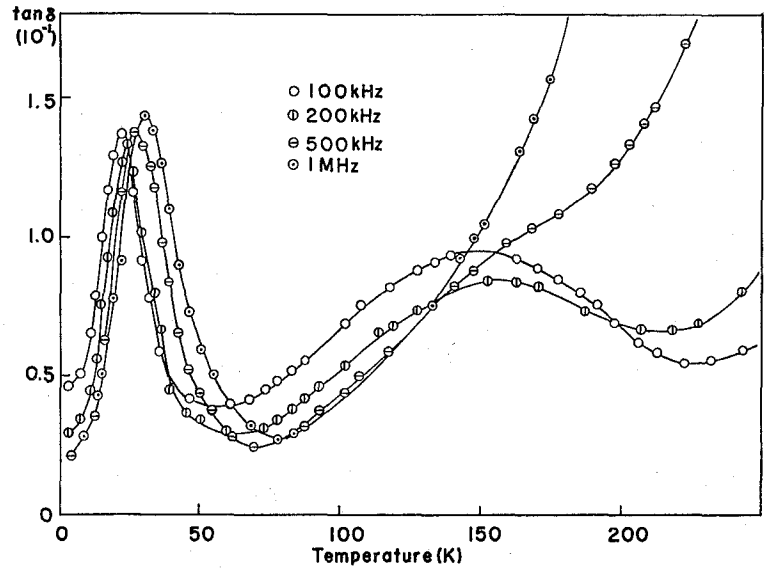


Fig. 5. (a) Temperature dependence of permeability of $Mn_{0.47}Zn_{0.48}Fe_{2.05}O_4$.



(b) Temperature dependence of loss tangent of the same sample.

energies of 0.1–0.4 eV in these magnetic relaxations are in accord with those of d.c. electrical conductivity. But the measurement below liquid nitrogen temperature was not reported. S. Iida *et al.* reported the details of the electronic relaxation in $Mn_xFe_{3-x}O_{4+y}$.[9,10] They found the Richter type magnetic relaxation at 20~40 K in $Mn_xFe_{3-x}O_4$ for $x \leq 0.9$ and another loss peak above 100 K for $x \geq 0.6$. It was proposed that for Fe_3O_4 the lower temperature relaxation below 50 K is due to the electron transfer between four crystallographically equivalent iron ions ($2Fe^{2+}+2Fe^{3+}$) on the octahedral sites in the Verwey ordering of electrons. The relaxations observed for Fe_3O_4 and MnZn ferrites at 20–40 K in this work are considered to be produced by the same origin. This is supported by the result that the activation energy of the magnetic relaxation is in accord with that of conductivity (Table I), for the conductivity is determined by the electron transfer mechanism in these materials. The dielectric relaxation seen in Fe_3O_4 below 50 K has the activation energy of 0.05 eV in previous work[7] which is the same energy as shown in Table I. The acoustic loss of Fe_3O_4 single crystal has a peak at about 50 K corresponding to the magnetic and dielectric relaxations. The activation energy of the acoustic relaxation is 0.55 eV[11] coincident with the activation energy mentioned above for magnetic and dielectric relaxations. Hence it is concluded that these magnetic, dielectric and acoustic loss are originated in the same relaxation mechanism (electron transfer or electron hopping mechanism). Since the peak in acoustic loss is not seen in stoichiometric Fe_3O_4 but only in slightly oxidized Fe_3O_4, S. Iida pointed out that the ion sites which contribute to the relaxation are associated with cation vacacies.[12]

The magnetic relaxation observed at 163 K for MnZn ferrites shows a broader peak than the one at 30 K. The former has the wider distribution of relaxation times. Moreover, the increase of eddy current loss arising from high conductivity makes the peak vague. The Jahn-Teller distortion occurs in $Mn_xFe_{3-x}O_4$ and in MnZn ferrite. S. Iida assigned this peak to the dynamical Jahn-Teller distortion. Variation of the reorientational frequency ω_R of the distortion with temperature is given by

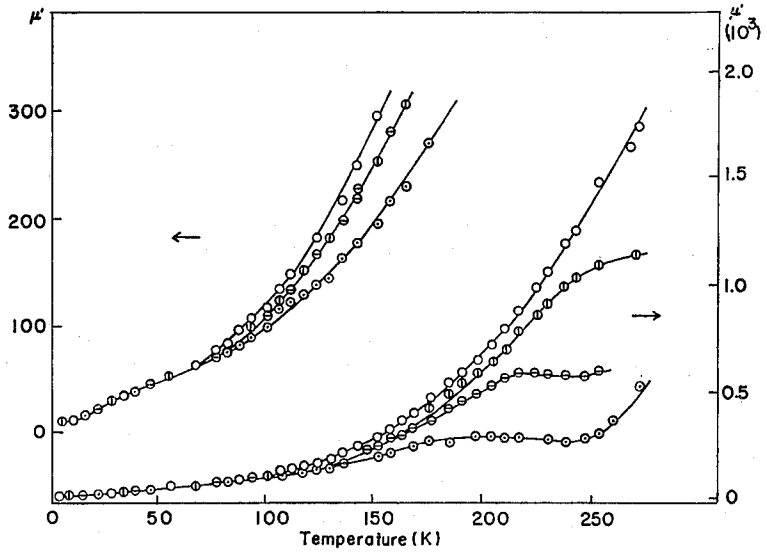
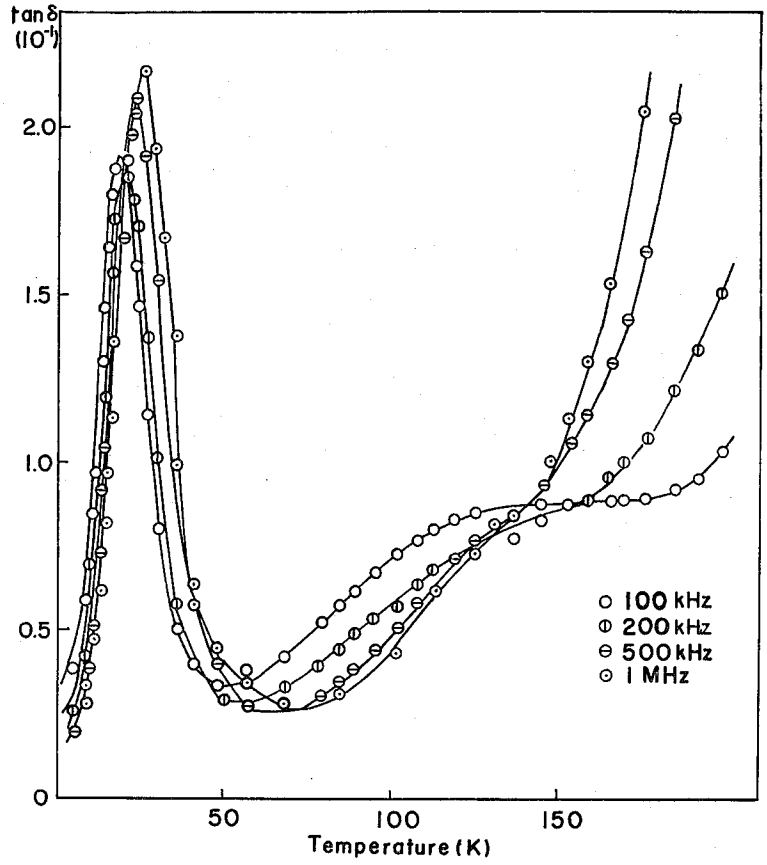


Fig. 6. (a) Temperature dependence of permeability of $Mn_{0.63}Zn_{0.31}Fe_{2.06}O_4$.



(b) Temperature dependence of loss tangent of the same sample.

Table I Comparison of Activation Energy (eV)

	Conductivity	Magnetic relaxation
Fe_3O_4	4×10^{-2}	5.7×10^{-2}
$Mn_{0.47}Zn_{0.48}Fe_{2.05}O_4$	1.1×10^{-2}	1.6×10^{-2}
$Mn_{0.63}Zn_{0.31}Fe_{2.06}O_4$	7.6×10^{-3}	1.3×10^{-2}

$$\omega_R=\omega_0 \exp\left(\frac{-V}{kT}\right) \tag{11}$$

where ω_0 is the frequency of lattice vibration and V is the activation energy of the distortion. When the reorientational frequency is equal to the observing frequency of a.c. permeability measurement the absorption of energy will be the maximum. Though this peak is considered to be related with Mn ions the detailed mechanism is not known.

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